## as originally filed

## Liquid-crystalline media comprising polymers

The present invention provides liquid crystal media, in particular having low birefringence, for use in liquid crystal display systems (displays). These liquid crystal display systems include screens of televisions, computers, e.g. notebook computers or desktop computers, switching centers and of other instruments, e.g. amusement arcade machines, electrooptical displays such as displays of watches, pocket calculators, electronic (pocket) games, transportable data stores such as PDAs (personal digital assistants) or of mobile telephones.

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The liquid crystal switching elements which are typically used in such liquid crystal displays are the known TN (twisted nematic) switching elements, for example according to Schadt, M. and Helfrich, W. Appl. Phys. Lett. 18, p. 127 ff. (1974), and in particular in their specific form having short visual delay d·Δn in the range from 150 nm to 600 nm according to DE 30 22 818, STN (supertwisted nematic) switching elements, for example according to GB 2 123 163, DE 34 31 871, DE 36 08 911 and EP 0 260 450, IPS (in-plane switching) switching elements, as described, for example, in DE 40 00 451 and EP 0 588 568, and VAN (vertically aligned nematic) switching elements, as described in Tanaka, Y. et al., K. SID 99 Digest p. 206 ff (1999), Koma et al., International Display Workshop (IDW) '97 p. 789 ff (1997) and Kim et al., Asia Display 98, p. 383 ff, (1998).

The visual appearance of these existing liquid crystal display devices, which are for the most part already commercially available, is unsatisfactory, at least for demanding applications. In particular, the contrast, especially in color reproductions, the brightness, the color saturation and the viewing angle dependence of these leading examples are capable of being distinctly improved. Further disadvantages of liquid crystal display devices are often their lack of spatial resolution and inadequate switching times, in particular in the cases of STN switching elements, but also in the case of TN switching elements or IPS (in-plane switching) and VAN (vertically aligned nematic) switching elements, and, in the case of the latter in particular, when these are to be used for reproducing video, for instance in multimedia applications on computer screens or in televisions. For this purpose in particular, but even for the display of rapid cursor movements, short

switching times, preferably of less than 32 ms, more preferably of less than 16 ms, are desired.

The requirements in the viewing angle dependence of the contrast depend to a large extent on the use of the display devices. For example, in the case of television screens and computer monitors, it is the horizontal viewing angle region which is most important, whereas centrosymmetric viewing angle distributions are desired in other applications. In general, it is to be noted that the primary criterion for practical acceptance of a display is not its contrast or its maximum contrast ratio, but rather the viewing angle dependence of the contrast. However, these properties have to be given different weights depending on the application.

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TN switching elements having  $d \cdot \Delta n$  in the range from  $0.2 \, \mu m$  to  $0.6 \, \mu m$ , as described in DE 30 22 818, generally have very good color saturation and color depth, but an unsatisfactory viewing angle range for demanding applications, for example computer monitors for desktop computers.

WO 01/07962 describes liquid crystal switching elements comprising at least one polarizer and a liquid crystal layer which has a starting alignment in which the liquid crystal molecules are aligned substantially parallel to the substrates and substantially parallel to each other, and in which the realignment of the liquid crystals from their starting alignment, which is substantially parallel to the substrates, is brought about by an appropriate electrical field which, in the case of liquid crystal materials having negative dielectric anisotropy, is aligned parallel to the substrates and, in the case of liquid crystal materials having positive dielectric isotropy, is substantially perpendicular to the substrates. In this case, the liquid crystal layer has an extremely low visual delay d- $\Delta$ n in the range from 0.06  $\mu$ m to 0.43  $\mu$ m and the liquid crystal switching element, in addition to the liquid crystal layer, preferably has a further birefringent layer, preferably one  $\lambda$ /4 layer or two  $\lambda$ /4 layers or one  $\lambda$ /2 layer. The liquid crystal display systems comprising such liquid crystal switching elements are also described.

The liquid crystal switching elements described in WO 01/07962 do not have the disadvantages of the existing switching elements, or at least to a distinctly reduced extent. They feature very good contrast coupled with simultaneously outstanding viewing angle dependence of the contrast. They permit the representation both of shades of gray and also half-tone colors over a wide range of viewing angles.

However, the switching times of these liquid crystal switching elements are still in need of improvement.

It is an object of the present invention to provide suitable liquid-crystalline media which result in liquid crystal switching elements having distinctly reduced switching times.

This object is achieved by a medium comprising

- a) one or more liquid-crystalline compounds and
- 10 b) polymers composed of one or more polymerizable compounds of the general formula (I)

$$P^{1}-Sp^{1}-X^{1}-A^{1}-(Z^{1}-A^{2})_{n}-R$$
 (I)

where:

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R is H, F, Cl, CN, SCN, SF<sub>5</sub>H, NO<sub>2</sub>, straight-chain or branched alkyl having from 1 to 12 carbon atoms, of which one or two nonadjacent CH<sub>2</sub> groups may be replaced by -O-, -S-, -CH=CH-, -CO-, -COO-, -COO-, -O-COO-, -S-CO-, -CO-S-, -CH=CH- or -C≡C- in such a way that oxygen and/or sulfur atoms are not directly bonded together, or -X<sup>2</sup>-Sp<sup>2</sup>-P<sup>2</sup>,

- 25 P and  $P^2$  are each independently a polymerizable group, preferably  $-O(CO)-(CH_2)_0-CH=CH_2$ ,  $-O(CO)-CH=CH-(CH_2)_p-H$ ,  $-CH=CH-(CH_2)_q-H$ , or  $-O(CO)-C(CH_3)=CH-(CH_2)_r-H$  where o, p, q, r = 0-8,
- 30 Sp<sup>1</sup> and Sp<sup>2</sup> are each independently a spacer group, preferably  $-(CH_2)_{m}$ where m = 1-8, or a single bond,
- are each independently -O-, -S-, -OCH<sub>2</sub>-, -CH<sub>2</sub>O-, -CO-, -COO-, -OCO-, -OCO-O, "-CO-NR<sup>0</sup>-, -NR<sup>0</sup>-CO-, -OCH<sub>2</sub>-, -CH<sub>2</sub>O-, -SCH<sub>2</sub>-, -CH<sub>2</sub>S-, -CH=CH-COO-, -OOC-CH=CH-or a single bond,
  - A<sup>1</sup> and A<sup>2</sup> are each independently 1,4-phenylene in which one or more CH groups may be replaced by N, 1,4-cyclohexylene in

which one or more nonadjacent CH<sub>2</sub> groups may be replaced by O and/or S, 1,4-cyclohexenylene, 1,4bicyclo(2,2,2)octylene, piperidine-1,4-diyl, naphthalene-2,6diyl, decahydronaphthalene-2,6-diyl, 1,2,3,4-tetrahydronaphthalene-2,6-diyl or indane-2,5-diyl, and all these groups may be unsubstituted or mono- or polysubstituted by L,

L is F, Cl, CN or alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl or alkylcarbonyloxy having from 1 to 7 carbon atoms, in which one or more hydrogen atoms may be replaced by F or Cl,

Z¹ is -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, -OCH<sub>2</sub>-, -CH<sub>2</sub>O-, -SCH<sub>2</sub>-, -CH<sub>2</sub>S-, -CF<sub>2</sub>O-, -OCF<sub>2</sub>-, -CF<sub>2</sub>-S-, -SCF<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-, -CF<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>-CF<sub>2</sub>-, -CF<sub>2</sub>-CF<sub>2</sub>-, -CH=CH-, -CF=CF-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH-, CR<sup>0</sup>R<sup>00</sup> or a single bond, and

 $R^0$  and  $R^{00}$  are each independently H or alkyl having from 1 to 4 carbon atoms,

n is 0, 1 or 2.

It has been found that doping the liquid-crystalline media with the compounds of the formula (I) which form a polymeric network and subsequently effecting polymerization with UV induction provides liquid-crystalline media having distinctly reduced switching times.

Preferred liquid-crystalline media comprise polymerizable compounds selected 30 from the following formulae

$$P^1$$
  $O$   $P^2$  (Ia)

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$$P^1$$
  $O$   $O$   $P^2$  (Ic)

$$P^{1}((CH_{2})_{m1}-O)_{r1}$$
  $O$   $Z^{2}$   $O$   $Z^{3}$   $O$   $O$   $(O-(CH_{2})_{m2})_{r2}-P^{2}$  (Id)

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$$P^1 \longrightarrow O \longrightarrow P^2$$
 (If)

$$P^{1} \longrightarrow P^{2} \qquad (Ig)$$

$$P^{1} \longrightarrow \begin{array}{c} F \\ O \\ \end{array} \longrightarrow P^{2} \qquad \text{(Ih)}$$

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where P<sup>1</sup> and P<sup>2</sup> are each as defined above, Z<sup>2</sup> and Z<sup>3</sup> are each independently as defined for Z<sup>1</sup>, m1 and m2 are each independently from 1 to 8, r1 and r2 are each independently 0 or 1, and R<sup>a</sup> and R<sup>b</sup> are each independently H or CH<sub>3</sub>, and L<sup>1</sup> is H or -CH<sub>3</sub>.

In these formulae,  $P^1$  and  $P^2$  are preferably each independently selected from

 $-O(CO)-(CH_2)_0-CH=CH_2$ ,  $-O(CO)-CH=CH-(CH_2)_0-H$ ,  $-CH=CH-(CH_2)_0-H$ , where o, p, q = 0-8,

5 Particularly preferred polymerizable compounds are the following compounds (Ij)-(Im):

15 (lm)

> The present invention further provides mixtures for producing the liquidcrystalline media comprising

- 20 a) one or more liquid-crystalline compounds,
  - b) one or more compounds of the general formula I,
  - c) optionally one or more polymerization initiators, preferably photoinitiators.

The compounds of the general formula (I) are typically present in amounts of from 25 0.1 to 1% by weight, preferably from 0.2 to 0.5% by weight. Suitable photoinitiators are, for example, Irgacure 651 from Ciba. These are present, based on the compounds to be polymerized, typically in amounts of from 1 to 10% by weight, preferably from 2 to 4% by weight. The liquid-crystalline media according to the invention can be obtained by UV irradiation of these precursor mixtures. Irradiation is effected typically using light of a wavelength between 300 and 30 500 nm.

The liquid-crystalline media according to the invention preferably comprise from 3 to 27, more preferably from 10 to 21 and most preferably from 12 to 18 single compounds. The single compounds used with preference preferably each contain a 1,4'-trans-trans-bicyclohexylene unit of the partial formula i:

$$-$$
Z $-$ [ $-$ ]<sub>n</sub> (i)

where

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10 Z is a single bond, -CH<sub>2</sub>CH<sub>2</sub>- or -CF<sub>2</sub>-CF<sub>2</sub>-, and

n is 1 or 2.

In this unit, one or preferably two nonadjacent -CH<sub>2</sub>- groups in one of the cyclohexane rings may be replaced by oxygen atoms, or two adjacent -CH<sub>2</sub>- groups may be replaced by one -CH=CH- group.

In the case of compounds having only two six-membered rings overall, one of the two cyclohexane rings may optionally be replaced by unsubstituted or optionally doubly, or preferably singly, laterally fluorinated 1,4-phenylene.

The liquid crystal mixtures preferably comprise one or more compounds having a structural unit of the formula i where n = 2.

The liquid crystal mixtures used in the liquid crystal switching elements according to the invention preferably comprise

- a component A consisting of compounds having two six-membered rings,
- a component B consisting of compounds having three six-membered rings and optionally
- 30 a component C consisting of compounds having four six-membered rings.

The liquid crystal mixtures preferably consist substantially of components A, B and optionally C.

- 35 Particularly preferred liquid crystal mixtures comprise one or more
  - dielectrically neutral compounds of the formula II

$$R^{11}$$
  $R^{12}$  (II)

where

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R<sup>11</sup> is n-alkyl having from 1 to 5 carbon atoms,

R<sup>12</sup> is n-alkyl having from 1 to 5 carbon atoms, 1E-alkenyl, preferably vinyl, or n-alkoxy having from 1 to 6 carbon atoms,

optionally, dielectrically positive compounds selected from the group of the formulae III and III'

$$R^{21}$$
  $Z^4$   $X^3$  (III)

15 where

R<sup>21</sup> is n-alkyl or 1E-alkenyl having from 3 to 7 and from 2 to 8, preferably from 5 to 7 and from 4 to 6, carbon atoms respectively,

20 Z<sup>4</sup> is a single bond or -CH<sub>2</sub>CH<sub>2</sub>-

and

X<sup>3</sup> is OCF<sub>3</sub>, CF<sub>3</sub> or CH<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub>, preferably CF<sub>3</sub> or CH<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub>,

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$$R^{21} \longrightarrow Z^{4} \longrightarrow Q \longrightarrow X^{4}$$
 (III')

where

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R<sup>21</sup> is n-alkyl or 1E-alkenyl having from 3 to 7 and from 2 to 8, preferably from 5 to 7 and from 4 to 6, carbon atoms respectively,

 $Z^4$  is a single bond or -CH<sub>2</sub>CH<sub>2</sub>-,

X<sup>4</sup> is OCF<sub>2</sub>H, OCF<sub>3</sub> or F, preferably F,

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and

Y<sup>2</sup> is in each case independently H or F,

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compounds of the formula IV

$$R^{31} - Z^{32} - Z^{32} - Z^{32} - Z^{31}$$
 (IV)

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where

R<sup>31</sup> is n-alkyl or 1E-alkenyl having from 2 to 7, preferably from 2 to 5, carbon atoms,

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 $Z^{31}$  and  $Z^{32}$  are each a single bond, -CH<sub>2</sub>CH<sub>2</sub>- or -CF<sub>2</sub>CF<sub>2</sub>-, preferably -CH<sub>2</sub>CH<sub>2</sub>-, but more preferably each a single bond,

 $X^5$  is OCF<sub>2</sub>H, OCF<sub>3</sub> or F,

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Y<sup>3</sup> is in each case independently H or F,

in the case that

 $X^5 = OCF_2H$ , both  $Y^3$  are preferably F,

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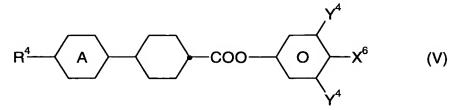
in the case that

 $X^5 = F$ , both  $Y^3$  are preferably F,

in the case that

35  $X^5 = OCF_3$ , one  $Y^3$  is preferably F, the other H,

optionally, one or more compounds from the group of compounds of the formulae V and VI



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where

R<sup>4</sup> is n-alkyl or 1E-alkenyl having from 2 to 5, preferably having from 2 to 5, carbon atoms,

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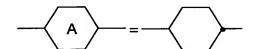
X<sup>6</sup> is OCF<sup>2</sup>H, OCF<sup>3</sup> or F, preferably F or OCF<sup>3</sup>,

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Y<sup>4</sup> is in each case independently H or F,

in the case that

X=F and



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both Y<sup>4</sup> are preferably F,

in the case that

 $X = OCF^3$  and more preferably in the case that

one Y<sup>3</sup> is F, the other H,

$$R^{5} \longrightarrow C \longrightarrow Z^{5} \longrightarrow C \longrightarrow X^{7} \qquad (VI)$$

where

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R<sup>5</sup> is n-alkyl or 1E-alkenyl having from 2 to 5 carbon atoms,

Z<sup>5</sup> is a single bond or -CH<sub>2</sub>CH<sub>2</sub>-,

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X<sup>7</sup> is F, OCF<sub>3</sub> or OCF<sub>2</sub>H,

Y<sup>5</sup> is in each case independently H or F,

preferably,

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$$X^7, Y^5 = F,$$

optionally, one or more compounds which have a high clearing point and are selected from the group of compounds of the formulae VII to X

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$$R^{61}$$
  $COO$   $R^{62}$  (VII)

$$R^{71}$$
  $CH_2O$   $R^{72}$  (VIII)

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$$R^{81} \longrightarrow COO \longrightarrow CO \longrightarrow R^{82} \qquad (IX)$$

$$R^{91} \longrightarrow O \longrightarrow R^{92} \qquad (X)$$

$$R^{10}$$
  $O$   $Y^{10}$   $X^{10}$   $X^{10}$ 

$$R^{11} \longrightarrow O \longrightarrow X^{11} \qquad (XII)$$

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where  $R^{71}$  and  $R^{72}$ ,  $R^{81}$  and  $R^{82}$ ,  $R^{91}$  and  $R^{92}$ ,  $R^{10}$  and also  $R^{11}$  are each independently as defined above for  $R^{11}$  and  $R^{12}$ ,

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L<sup>81</sup>, L<sup>91</sup> are each H or F and

 $X^{10}$ ,  $Y^{10}$  and also  $X^{11}$ ,  $Y^{11}$  are each independently as defined above for  $X^5$ ,  $Y^3$ ,

15 and

optionally, one or more compounds of the formula (XIII)

$$R^{13} \longrightarrow CF_2O \longrightarrow CF_2O \longrightarrow X^{13} \qquad (XIII)$$

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where  $R^{13}$ ,  $X^{13}$  and  $Y^{13}$  are each independently as defined above for  $R^{11}$ ,  $X^5$  and  $Y^3$  respectively, and

$$-\sqrt{A^{13}}$$
 is  $-\sqrt{O}$  or  $-\sqrt{O}$ 

preferably

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The liquid crystal mixtures according to the present application preferably comprise from 4 to 36 compounds, more preferably from 6 to 25 compounds and most preferably from 7 to 20 compounds.

The present invention also provides an electrooptical liquid crystal switching element comprising at least one polarizer and a liquid crystal layer which has a starting alignment in which the liquid crystal molecules are aligned substantially parallel to the substrates and substantially parallel to each other, and in which the realignment of the liquid crystals from their starting alignment, which is substantially parallel to the substrates, is brought about by an appropriate electrical field which, in the case of liquid crystal materials having negative dielectric anisotropy, is aligned parallel to the substrates and, in the case of liquid crystal materials having positive dielectric isotropy, is substantially perpendicular to the substrates, said liquid crystal layer comprising the liquid-crystalline medium according to the invention. The liquid crystal layer preferably has an extremely low visual delay d·Δn in the range from 0.06 μm to 0.43 μm and the liquid crystal switching element, in addition to the liquid crystal layer, preferably has a further birefringent layer, preferably one  $\lambda/4$  layer or two  $\lambda/4$  layers or one  $\lambda/2$  layer. The present invention further provides liquid crystal display systems comprising such liquid crystal switching elements.

The liquid crystal display systems according to the invention are very suitable in particular for applications involving reproduction in shades of gray, for example televisions, computer monitors and multimedia devices.

The liquid crystal switching elements of the present invention comprise a liquid crystal layer having preferably short visual delay, optionally a further birefringent layer, preferably one  $\lambda/4$  layer, one  $\lambda/2$  layer or two  $\lambda/4$  layers, and also at least one polarizer. The two  $\lambda/4$  layers may replace the  $\lambda/2$  layer.

The transmissive or transflective liquid crystal switching elements preferably comprise a polarizer and an analyzer which are arranged on opposite sides of the arrangement of liquid crystal layer and birefringent layer. In this application, polarizer and analyzer are referred to together as polarizers. The construction of the liquid crystal switching elements is described in principle in WO 01/07962, see in particular Fig. 1a, 1b and 2.

The liquid crystal layer is typically secured between two substrates. At least one of the substrates is transparent, and both substrates are preferably transparent. The transparent substrates consist, for example, of glass, quartz glass, quartz or of transparent plastics, preferably of glass and more preferably of borosilicate glass.

The substrates together with an adhesive frame form a cell in which the liquid crystal material of the liquid crystal layer is secured. The substrates are preferably planar.

The spacing of the flat substrates is kept substantially constant over the entire surface by means of spacers.

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The preferred substrate thicknesses are from 0.3 mm to 1.1 mm, more preferably from 0.4 mm to 0.7 mm. In the case of the larger diagonals of the cells, preference is given to using the substrates having the larger thicknesses.

The liquid crystal switching elements according to the invention feature very good capacity for gray shades, a low dependence of the contrast on the viewing angle even in color displays, a large viewing angle range and low contrast inversion, and also in particular very short switching times. In particular, inverse contrast, as defined in DE 42 12 744, which occurs, for example, in displays according to DE 30 22 818, is distinctly reduced at relatively large viewing angles θ in particular.

In the case that they are reflective switching elements, the liquid crystal switching elements of the present invention have at least one polarizer and one reflector, and at least one polarizer and the reflector are disposed on the mutually opposite sides (i.e. substrates) of the liquid crystal cells. In the case that they are transmissive or reflective switching elements, they preferably have at least two polarizers of which in each case at least one is disposed on one of the two opposite sides of the liquid crystal cells (sandwich structure). The obligatory polarizers mentioned are

preferably linear polarizers and more preferably linear polarizers having a high degree of polarization.

In addition to the obligatory polarizers, the switching elements according to the invention may comprise one or more further polarizers. These may be cleanup polarizers having a relatively low degree of polarization but high transmission. However, in the case of reflective switching elements, a further polarizer having a high degree of polarization may also be present. This is preferably disposed between the liquid crystal cell and the reflector. However, the use of additional polarizers is generally less preferred, since they lead in most cases to a reduction in transmission. However, it is customary in particular in combination with brightness-increasing components which may comprise, for example, cholesteric polymer films.

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In the case of the transmissive and transflective displays of the present application, the two obligatory polarizers are either in crossed or parallel arrangements. In this application, the directions of the orientation of the polarizers are based on their absorption axes. Preference is given to the crossed arrangement of the polarizers. The angle of the absorption axes relative to each other (Ψ<sub>pp</sub>) in the case of crossed polarizers is from 75°C to 105°C, in particular approx. 90°, and in the case of parallel polarizers, from -15° to 15°, in particular approx. 0°.

The angle between the absorption axis of the polarizer adjacent to the liquid crystal layer with the direction of orientation of the director of the liquid crystal layer in the unswitched (field-free) state at the adjacent substrate ( $\Psi_{PL}$ ) is from 35° to 55° and ideally 45°. This applies to untwisted alignments of the liquid crystal. In the case of the twisted alignment of the liquid crystal, the basis direction for the specification of the angle  $\Psi_{PL}$  is the projection of the orientation of the liquid crystal director midway between the two substrates of the cell to the substrate adjacent to the polarizer. When further birefringent layers and/or compensators are used in addition to the  $\lambda/4$  or  $\lambda/2$  layers, which are obligatory or preferred depending on the embodiment, other angles between polarizer direction and liquid crystal alignment can also be used. However, these are generally not preferred.

35 The tilt angle ( $\phi$ ) of the liquid crystal layer between the two substrates, in particular in the case of switching elements having one birefringent layer, in particular having a  $\lambda/4$  or  $\lambda/2$  layer, or having a plurality of birefringent layers, in particular having two  $\lambda/4$  layers, is preferably from  $-20^{\circ}$  to  $20^{\circ}$ , more preferably

from  $-10^{\circ}$  to  $10^{\circ}$ , especially preferably from  $-5^{\circ}$  to  $5^{\circ}$ , even more preferably from  $-2^{\circ}$  to  $2^{\circ}$  and most preferably from  $-1^{\circ}$  to  $1^{\circ}$ .

For the preferred embodiments without birefringent layer, i.e. without  $\lambda 4$  or  $\lambda 2$  layer or layers, the liquid crystal layer is substantially untwisted and more preferably untwisted. Preference is given to a twist angle ( $\phi$ ) of from  $-6^{\circ}$  to  $6^{\circ}$ . Particular preference is given to a twist angle being from  $-1.0^{\circ}$  to  $1.0^{\circ}$ , very particularly preferably from  $-0.5^{\circ}$  to  $0.5^{\circ}$ , especially preferably  $0.0^{\circ}$ .

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The alignment of the liquid crystal materials to the substrate surfaces is effected by customary processes. To this end, inclined vapor deposition with inorganic compounds, preferably oxides such as SiO<sub>x</sub>, alignment on surfaces rubbed in an antiparallel manner, in particular polymer layers such as polyamide layers which have been rubbed in an antiparallel manner, or alignment on photopolymerized anisotropic polymers are used. In the case of vertical alignment (VA), lecithin or surface-active materials can also be used for homeotropic alignment.

The surface tilt angle at the substrates ( $\phi_0$ , also known as tilt angle or tilt for short) is in the range from 0° to 15°, preferably in the range from 0° to 10°, more preferably in the range from 0.1° to 5° and especially preferably in the range from 0.2° to 5° and most preferably in the range from 0.3° to 3°. The surface tilt angle at the alignment layer on at least one of the substrate surfaces is from 0.5° to 3°. The tilt angle on both substrates is preferably substantially identical.

- The electrodes on the substrates are, at least on one of the substrates and preferably on both substrates, transparent. The material used for the electrodes is preferably indium tin oxide (ITO), although aluminum, copper, silver and/or gold can also be used.
- 30 Since the surface tilt angle in the liquid crystal display elements according to the invention may be small, the use of anisotropically photopolymerizable materials, for example cinnamic acid derivatives, known as photoalignment, can be used with particular advantage.
- This is true especially for a preferred embodiment of the liquid crystal display elements according to the invention having multidomain switching elements. In this case, the individual liquid crystal switching elements or their individual display electrodes (also known as pixels) in subregions having different alignment

of the liquid crystal director at least in the switched state, but generally also in the unswitched state, known as domains.

The active electrical switching elements of the active matrix used are both two-pole structures such as diodes, e.g. MIM diodes or back-to-back diodes, optionally with reset, and three-pole structures such as transistors, e.g. thin-film transistors (TFTs) or varistors. For the liquid crystal display devices of the present application, preference is given to TFTs. The active semiconductor medium of these TFTs is amorphous silicon (a-Si), polycrystalline silicon (poly-Si) or cadmium selenide (CdSe), preferably a-Si or poly-Si. In this context, poly-Si refers equally to high temperature and low temperature poly-Si.

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In liquid crystal switching elements in a preferred embodiment of the present invention, the liquid crystal layer preferably has a visual delay (d· $\Delta n$ ) of from 0.14  $\mu m$  to 0.42  $\mu m$ , more preferably from 0.22  $\mu m$  to 0.34  $\mu m$ , especially preferably from 0.25  $\mu m$  to 0.31  $\mu m$ , even more preferably from 0.27  $\mu m$  to 0.29  $\mu$  and ideally 0.28  $\mu m$ .

For this purpose, preference is given to using liquid crystal materials having low birefringence Δn. The birefringence of the liquid crystal materials is preferably from 0.02 to 0.09, more preferably from 0.04 to 0.08, especially preferably from 0.05 to 0.075, even more preferably from 0.055 to 0.070 and ideally from 0.060 to 0.065.

In the case of liquid crystal display devices having liquid crystal cells having a diagonal of up to 6", preference is given to layer thicknesses of the liquid crystal layer of from 1 μm to 4 μm and particularly from 2 μm to 3 μm. In the case of liquid crystal display devices having liquid crystal cells having a diagonal from 10", preference is given to layer thicknesses of the liquid crystal layer of from 3 μm to 6 μm and particularly from 4 μm to 5 μm.

For this preferred embodiment, there are two different preferred subforms.

In the first of these preferred subembodiments of the present invention, the liquid crystal layer has a visual delay (d· $\Delta$ n) of from 0.20  $\mu$ m to 0.37  $\mu$ m, preferably from 0.25  $\mu$ m to 0.32  $\mu$ m, more preferably from 0.26  $\mu$ m to 0.30  $\mu$ m, even more preferably from 0.27  $\mu$ m to 0.29  $\mu$ m, and most preferably of 0.28  $\mu$ m.

In this preferred subembodiment, the display element in some applications surprisingly requires no  $\lambda/4$  layer. In spite of this, when the polarizer is positioned appropriately, preferably at an angle of substantially 45° to the preferred liquid crystal direction, it is characterized by good brightness, outstanding contrast and excellent viewing angle dependency and very good shades of gray, and also reproduction of color hues. Without a  $\lambda/4$  layer, a very broad viewing angle range is achieved for the viewing angle  $\Theta$ , but not for the viewing angle  $\Phi$ . In contrast, the viewing angle range in the case of the switching elements having a  $\lambda/4$  layer is distinctly more centrosymmetric, i.e., at all viewing angles  $\Phi$ , extends to similar, large values of the viewing angle  $\Theta$ .

In the second of these preferred subembodiments of the present invention, the display elements preferably comprise a  $\lambda/4$  layer and the liquid crystal layer has a visual delay [ $(d\cdot\Delta n)_{LC}$ ] of from 0.10 to 0.45  $\mu$ m, preferably from 0.20 to 0.37  $\mu$ m, more preferably from 0.25  $\mu$ m to 0.32  $\mu$ m, even more preferably from 0.26  $\mu$ m to 0.30  $\mu$ m, especially more preferably from 0.27  $\mu$ m to 0.29  $\mu$ m, and most preferably of 0.28  $\mu$ m. The liquid crystal layer in the unswitched state therefore behaves approximately like a  $\lambda/2$  layer. Preference is further given here to an embodiment in which the  $(d\cdot\Delta n)_{LC}$  is other than 0.28  $\mu$ m, and is preferably in the range from 0.10  $\mu$ m to 0.27  $\mu$ m or from 0.30  $\mu$ m to 0.45  $\mu$ m, more preferably from 0.14  $\mu$ m to 0.25  $\mu$ m or from 0.32  $\mu$ m to 0.42  $\mu$ m, even more preferably from 0.22  $\mu$ m to 0.25  $\mu$ m or from 0.32  $\mu$ m to 0.34  $\mu$ m.

In the present application, the wavelength  $\lambda$  is always based preferably on the wavelength of the maximum sensitivity of the human eye, at 554 nm, unless explicitly stated otherwise.

The terms  $\lambda/4$  layer and  $\lambda/4$  plate, and  $\lambda/2$  layer and  $\lambda/2$  plate, are generally used in the present application with the same meaning. The term  $\lambda$  in  $\lambda/4$  layer, and also  $\lambda/2$  layer, means a wavelength in the range of  $\lambda \pm 30\%$ , preferably  $\lambda \pm 20\%$ , more preferably  $\lambda \pm 10\%$ , especially preferably  $\lambda \pm 5\%$  and even more preferably  $\lambda \pm 2\%$ . In this context, unless stated otherwise, the wavelength is 554 nm. The wavelength of the  $\lambda/4$  layer or  $\lambda/2$  layer is generally, and especially in the case of a perceptible spectral distribution, specified as its central wavelength.

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The  $\lambda/4$  layer, or  $\lambda/2$  layer, is an inorganic layer or preferably an organic layer, for example of a birefringent polymer, for example stretched films (PET) or liquid-crystalline polymers.

Preference is given particularly to the smaller of the preferred layer thicknesses of the liquid crystal layer with regard to the advantageous short switching times achievable by. Furthermore, this allows the use instead of conventional liquid crystal materials or at least makes smaller requirements with regard to the often difficult realization of the small  $\Delta n$  values.

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In contrast, preference is given to the use of liquid crystal materials having particularly small  $\Delta n$  with regard to the relatively small layer thickness dependence of the contrast and of the background hue on the liquid crystal switching elements. Furthermore, particularly in the case of liquid crystal cells having relatively long diagonals, it is possible to produce display elements in this embodiment with distinctly greater yields.

For a wide working temperature range, particular preference is given to liquid crystal materials having a relatively high clearing point, since the effect of the  $\lambda/4$  layer, as a consequence of the temperature dependence of the birefringence of the liquid crystal materials  $[\Delta n_{LC}(T)]$ , is distinctly temperature-dependent, and  $\Delta n_{LC}(T)$  in the case of liquid crystal materials having a high clearing point is relatively low. The temperature dependence of the overall visual arrangement is thus kept relatively low and in this way can, where necessary, also be more easily compensated.

In a second preferred embodiment of the present invention, the liquid crystal layer has a visual delay of from  $0.07 \,\mu\text{m}$  to  $0.21 \,\mu\text{m}$ , preferably from  $0.11 \,\mu\text{m}$  to  $0.17 \,\mu\text{m}$ , more preferably from  $0.12 \,\mu\text{m}$  to  $0.16 \,\mu\text{m}$ , especially preferably from  $0.13 \,\mu\text{m}$  to  $0.15 \,\mu\text{m}$  and even more preferably of  $0.14 \,\mu\text{m}$ . In this preferred embodiment, the display element, in addition to the liquid crystal layer, preferably has at least one birefringent layer, preferably one  $\lambda/2$  layer or two  $\lambda/4$  layers.

30 To this end, preference is given to using liquid crystal materials having small birefringence  $\Delta n$ . The birefringence of the liquid crystal materials is preferably from 0.02 to 0.09, more preferably from 0.04 to 0.08, especially preferably from 0.05 to 0.07, even more preferably from 0055 to 0.065 and ideally approx. 0.060.

The layer thickness of the liquid crystal layer is generally from  $0.5 \,\mu m$  to  $7 \,\mu m$ , preferably from  $1 \,\mu m$  to  $5 \,\mu m$ , more preferably from  $1.5 \,\mu m$  to  $4 \,\mu m$  and especially preferably from  $2 \,\mu m$  to  $2.5 \,\mu m$ . In this context, preference is given in particular to displays having liquid crystal cells having relatively short diagonals, in particular in the range from 0.5" to 6", preferably in the range from 1" to 4".

In this second preferred embodiment, the liquid crystal switching elements preferably comprise two  $\lambda/4$  layers or more preferably one  $\lambda/2$  layer. The two  $\lambda/4$  layers may be used on different sides of the liquid crystal layer, but they may also be disposed on the same side of the liquid crystal layer.

Especially when the visual delay of the liquid crystal layer [ $(d \cdot \Delta n)_{LC}$ ] is distinctly different to 0.14  $\mu$ m, particularly when it is in the range from 0.07  $\mu$ m to 0.12  $\mu$ m or from 0.16  $\mu$ m to 0.21  $\mu$ m, it is necessary to use two  $\lambda/4$  layers or one  $\lambda/2$  layer.

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The liquid crystal switching elements of the present application may be operated transmissively, transflectively or reflectively. Preference is given to transmissive or transflective, particular preference to transmissive operation.

The reflectors used may be dielectric or metallic layers. Preference is given to metallic reflector layers. When metallic reflectors are used, a relatively large variation of the visual delay of the liquid crystal layer can be tolerated. When a dielectric mirror is used, the visual delay of the liquid crystal layer, especially in the case of switching elements without birefringent layer, is substantially λ/4.
When a second linear polarizer is used between the liquid crystal layer and the reflector, preference is given to using a dielectric reflector which preferably has a low proportion of depolarized reflection.

Particularly preferred parameter combinations are specified in WO 01/07962, tables 1 and 2.

The invention is illustrated in detail by the example which follows.

## Example

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The liquid-crystalline compounds are represented hereinbelow by acronyms.

In the acronyms, "C", "P", "D", "G", "U" and "Z" are defined as follows:

In addition,

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"n" 
$$R = -C_nH_{2n+1}$$

10 "V"  $R = -CH = CH_2$ 

"VI"  $R = -CH = CH - C_1H_{2l+1}$ 

"kVI"  $R = -C_kH_{2k} - CH = CH - C_1H_{2l+1}$ 

"IVk"  $R = -C_lH_{2l+1} - CH = CH - C_kH_{2k-1}$ 

"On"  $R = -OC_nH_{2n+1}$ 

15 "nO"  $R = -C_nH_{2n+1}O - C_nH_{2n+1}O - C_nH_{2n$ 

The substituent of the left-hand side of a structural formula is stated first and then, separated by a dash, the substituent of the right-hand side.

A liquid crystal switching element having antiparallel edge alignment and a polyamide alignment layer, a twist angle of  $0^{\circ}$  and a surface tilt angle of  $1.4^{\circ}$  was realized. The switching element comprised a  $\lambda/4$  layer and crossed polarizers which assumed an angle of  $45^{\circ}$  to the rubbing angle of the substrates. The

construction of the liquid crystal switching elements corresponds to the construction depicted in Figure 1 of WO 01/07962. The visual delay of the liquid crystal layer was  $0.277~\mu m$ . The composition of the liquid crystal layer used is reported in the table 1 which follows, together with the properties of the mixture as such, and also the characteristic voltages in the switching element.

Table 1

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Composition	% by wt.	Properties	
CC-3-O1	5.0	Transition T (S,N) < -30.0°C	
CCZC-3-3	3.0	Clearing point T (N, I) = $+68.0$ °C	
CCZC-3-5	3.0	$\Delta$ n (589 nm, 20°C) = +0.0602	
CCU-2-F	6.0	$\Delta \varepsilon (1 \text{ kHz}, 20^{\circ}\text{C}) = +10.3$	
CCZU-2-F	6.0	$\gamma_1 (20^{\circ}\text{C}) = 161 \text{ mPa·s}$	
CCZU-3-F	16.0	$d \cdot \Delta n = 0.277 \ \mu m$	
CCZU-5-F	6.0	Twist = $0^{\circ}$ C	
CDU-2-F	10.0		
CDU-3-F	12.0	$V_{10} (20^{\circ}C) = 1.22 \text{ V}$	
CDU-5-F	8.0	$V_{50} (20^{\circ}C) = 1.47 \text{ V}$	
CC-3-T	9.0	$V_{90} (20^{\circ}C) = 1.85 \text{ V}$	
CC-5-T	12.0		
CCPC-3-4	<u>4.0</u>		
$\Sigma$	<u>100.0</u>		

The mixture of table 1 was doped in the different concentrations specified in table 2 of the compounds Ij as a polymerizable compound and 2% of Irgacure 651 UV initiator. After filling the E/O cells, polymerization was effected by irradiating with a UV lamp (peak wavelength 375 nm, irradiation intensity approx. 50 mW/cm<sup>2</sup>, 2 minutes).

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Subsequently, the switching times and electrooptical parameters were measured in the above-described construction. To measure the switching times, switching was effected from 0 to 10V. The results are compiled in the table 2 which follows.

Table 2

conc./%	V10	V90	V90/V10	Ton/msec.	Toff./msec.	Ton+off/msec
0	1.27	3.05	2.40	5.3	24.7	30
0.5	1.42	3.87	2.73	5.5	23.6	29.1
0.75	1.61	4.92	3.06	5.5	21.6	27.1
1	2.08	6.09	2.93	5.8	18.3	24.1

5 The total switching time T<sub>on</sub> + T<sub>off</sub> can be reduced by approx. 20% by adding 1% by weight of polymerizable compound Ij. Furthermore, the higher concentrations (0.75% and 1.0%) exhibit distinctly flatter e/o curves. The steepness parameter V<sub>90</sub>/V<sub>10</sub> is approx. 25% greater than without the addition of the polymer. This is especially advantageous for the control of shades of gray and for the reduction of the switching time of the shades of gray.